

Diffusive hydrogen motion in $\text{ZrBe}_2\text{H}_{0.56}$: A quasielastic neutron scattering study

R.L. Cappelletti^{a,*}, T.J. Udovic^a, Z. Chowdhuri^a, B.C. Hauback^b,
A.J. Maeland^b, R.M. Dimeo^a

^aNIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-8562, USA

^bInstitute for Energy Technology, P.O. Box 40, Kjeller, NO-2027 Norway

Abstract

In $\text{ZrBe}_2\text{H}_{0.56}$, Be planes are separated by hexagonal Zr planes in the AlB_2 structure with the H atoms occupying interstitial sites that form a honeycomb net in the Zr planes. The data from quasielastic neutron scattering above 500 K using two spectrometers covering a wide range of resolutions from 1 to 64 μeV can be fitted with a simple model using only two parameters for all momentum transfers at each temperature. The parameters are an elastic-like fraction and the hopping rate of a quasielastic contribution consisting of two-dimensional nearest-neighbor uncorrelated hopping among the partially occupied interstitial sites. The temperature dependence of the hopping rate follows an Arrhenius relation with an activation energy of 0.30 ± 0.02 eV.

Published by Elsevier B.V.

PACS: 78.70.Nx

Keywords: Metal hydride; Quasielastic neutron scattering; 2-D hopping

1. Introduction

Intermetallic ZrBe_2 crystallizes in the hexagonal AlB_2 structure with alternating planes of Zr and Be atoms. Zr occupies (0, 0, 0) in the unit cell. The Be atoms occupy (1/3, 2/3, 1/2) and (2/3, 2/3, 1/2) positions that lie on a honeycomb net. The structure of the hydrides ZrBe_2H_x depends on the H concentration, x , and temperature. The system can host up to $x = 1.5$. The system is interesting since H diffuses rapidly and also because the diffusion is apparently two-dimensional (2-D), i.e., largely confined to the interstitial sites of the Zr planes that also form a honeycomb net. In this paper, we describe incoherent quasielastic neutron scattering used to study the diffusive motion of H. We focus on a temperature regime (above 500 K) and sample concentration $x = 0.56$ in which the sample was found to be structurally in a single phase, that of ZrBe_2 .

2. Experimental procedures

The ZrBe_2 sample was prepared by arc melting, followed by pulverization, and hydriding at room temperature and atmospheric pressure to $\text{ZrBe}_2\text{H}_{1.5}$ (for details, see Ref. [1]). Subsequent controlled hydrogen removal by evacuation at 673 K reduced the H content to $x = 0.56 \pm 0.04$ as corroborated by neutron prompt γ activation analysis at NIST [2]. Refinement of a neutron powder pattern taken at 500 K gives $a = 3.8140$ Å and $c = 3.2755$ Å for the majority P6/mmm phase.

The 2.3-g sample was placed in an aluminum foil wrapper inserted into the 0.27-mm-thick annulus (chosen to give 90% neutron transmission to reduce multiple-scattering effects) of an aluminum sample can sealed under He. The can was mounted on a closed-cycle He refrigerator for measurements on the NIST high-flux backscattering spectrometer (HFBS). The dynamical range chosen for this experiment, ± 36 μeV , gives an elastic peak resolution of 1.0 μeV full-width at half-maximum (FWHM). In order to reduce the data to extract the sample spectra,

*Corresponding author. Tel.: +1 301 975 6221; fax: +1 301 921 9847.

E-mail address: ronald.cappelletti@nist.gov (R.L. Cappelletti).

measurements were also made with an empty sample can (6 h). A 9-h run on the sample at 50 K was made to establish a resolution functions for each detector group. Runs lasting 10 h were then made at increasing temperatures of 530, 560, and 580 K, and then at 570 K.

The same sample and can arrangement measured with the HFBS was used for measurements on the NIST disk chopper spectrometer (DCS). Data reduction required measurements of an empty sample can, a vanadium rod for detector normalization, and the fast neutron background. The majority of DCS measurements were made with an incident wavelength of 6 Å resulting in an elastic peak resolution of 63.9 μeV FWHM. Seven 9 h runs were made at various temperatures: 300 K (for instrumental resolution), 520, 530, 540, 550, 560, and 580 K. In addition, the DCS settings were changed to give an incident wavelength of 7 Å with a resolution at the elastic peak of 20.3 μeV FWHM for 2 h runs at 300 K (for instrumental resolution) and 580 K.

3. Theory

The structure suggests that the observed quasielastic scattering might be accounted for simply by an extension to the non-Bravais honeycomb net of the Chudley–Elliot [3] model of uncorrelated nearest-neighbor (n.n.) hopping among the partially occupied interstitial sites. Monte Carlo (MC) calculations show that correlation has little effect on the *lineshape* at this concentration. The hopping distance d between n.n. sites is $a/\sqrt{3}$, where a is the lattice parameter in the plane. At 500 K, $d = 2.2020$ Å. This value is used in subsequent data fitting, ignoring changes with temperature, which are thought to be less than 1%.

Following the development in Rowe et al. [4] modified for the 2-D honeycomb net, the incoherent scattering cross-section is proportional to

$$F_{\text{inc}} = \frac{1}{2\pi} \times \left[\frac{(1 + \cos(\phi))(r - |A|)}{\omega^2 + (r - |A|)^2} + \frac{(1 - \cos(\phi))(r + |A|)}{\omega^2 + (r + |A|)^2} \right],$$

where $A = r[e^{i\vec{Q} \cdot \vec{d}_1} + e^{i\vec{Q} \cdot \vec{d}_2} + e^{i\vec{Q} \cdot \vec{d}_3}]/3 = |A|e^{i\phi}$. In the above equations, r is the hopping rate ($r = 1/\tau$, where τ is the mean residence time: the model envisions H sitting and vibrating at interstitial sites for a time τ between jumps), and \vec{d}_j are the vectors connecting an interstitial site to its three symmetrically arrayed, equally spaced n.n. sites in the plane. There are two inequivalent sets of these vectors for this non-Bravais net, the one being simply the negatives of the other.

The above expression was averaged for this powder sample equally over all directions of \vec{Q} and convolved with the resolution function for each group of detectors of the appropriate spectrometer to compare with measured spectra. Besides quasielastic scattering, all measured spectra were found to contain an elastic-like scattering

contribution. 2-D scattering gives an elastic contribution precisely for \vec{Q} perpendicular to the H-containing planes. When F_{inc} is averaged uniformly over \vec{Q} directions for our powder sample and convolved with the resolution function, this elastic contribution was found to be insufficient to account for the observed elastic-like scattering.

Thus, in order to obtain good fits of the model to the measured spectra, an additional elastic-like term was necessary. Before convolving with the resolution function, the model is described by a scattering cross-section that is proportional to $f\delta(\omega) + (1 - f)F_{\text{inc}}$ where f is the elastic-like fraction, i.e., beyond the contribution included in F_{inc} . In analyzing the spectra, care was taken to exclude detectors for Q values in the vicinity of Bragg peaks, so that the observed elastic-like scattering could only arise from diffuse coherent scattering, expected to be small and Q -dependent, or incoherent scattering from H that appeared immobile on the time scale of the measurements. In fact, the elastic-like fraction f has been found to be both independent of Q and between 12% and 15% for the HFBS depending slightly on temperature, which suggests that it indeed arises mainly from an H component having much lower mobility than the diffusing component.

An alternative attempt to describe the scattering without including an elastic-like term is a two-state model that includes thermally activated trapping [5]. Extensive testing of this model did not lead to satisfactory fits. We conclude from this attempt that the elastic-like peak is likely due to deeper trapping at various kinds of defects.

A MC method was employed to check whether correlated hopping can be safely ignored. To test the effects of correlations on the measured lineshapes, we calculated the powder-averaged intermediate scattering function (ISF) as a function of MC step number. A plot of the ISF for various concentrations is shown in Fig. 1 where it is seen that the effect of correlations on the *shape* of the line becomes pronounced beyond $x = 0.9$, well above the present concentration, $x = 0.56$. Since correlations are present in the actual system, the values of τ taken from fitting the dilute model to the data must already include the effects of both the blocking and correlation factors.

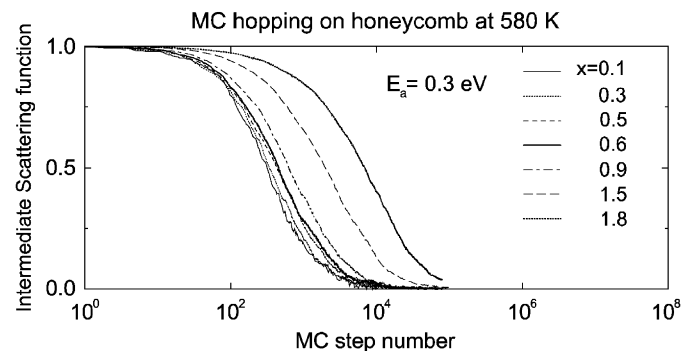


Fig. 1. Monte Carlo calculation of the ISF demonstrating the effect of correlated hopping.

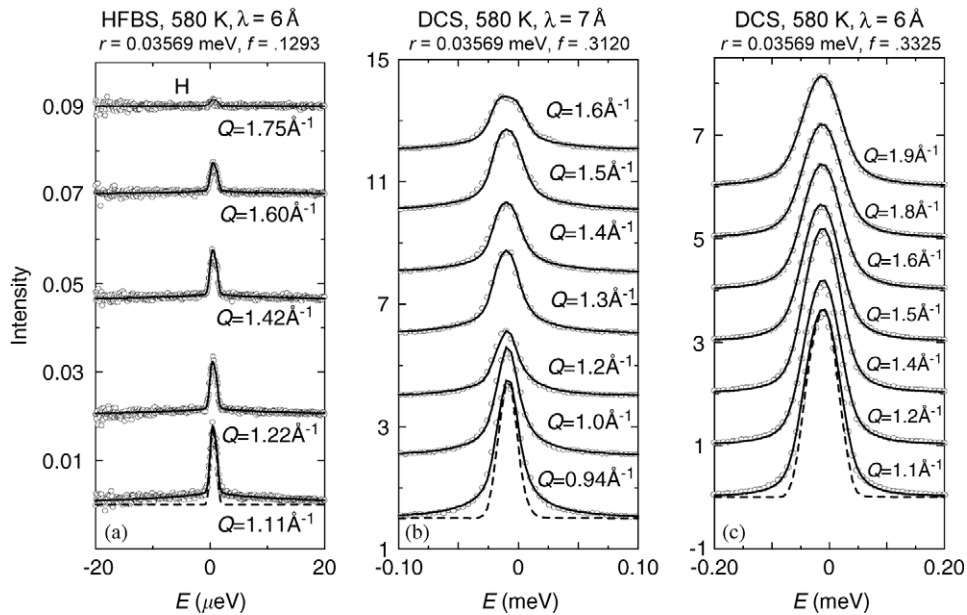


Fig. 2. Quasielastic spectra (arbitrarily shifted for clarity) at three resolutions: (a) 1 μeV , (b) 20 μeV , and (c) 64 μeV . Dotted lines are resolution functions at the indicated Q . Solid lines are the model fits.

Neither of these factors is temperature dependent, thus any systematic errors introduced by using a dilute-limit model to fit the data should not propagate into the temperature dependence of τ .

4. Results and discussion

The reduced data were fitted to the model described above using a specially adapted program within the DAVE data treatment suite available at the NCNR [6]. Data for the high Q HFBS spectra at 580 K are shown in Fig. 2a. Little correlation is found between the adjustable parameters r and f in fitting these HFBS data, and hence we regard the obtained values as being reliable.

The same program was used to treat DCS data after first restricting the spectrum to $\pm 0.7 \text{ meV}$ for the 7 \AA ($\approx 20 \mu\text{eV}$ resolution) data and to $\pm 1.3 \text{ meV}$ for the 6 \AA ($\approx 64 \mu\text{eV}$ resolution) data. In fitting the DCS data, a strong correlation was found between the fitting parameters r and f , rendering their independent determination unreliable. Since the fit in the wings is determined mainly by r , an alternative procedure is to take the r parameter from HFBS data and to fit the DCS data by letting f vary. DCS data for the high Q spectra at 580 K are shown in Fig. 2b and c for 20 and 64 μeV resolutions, respectively. The f values vary by a factor of ~ 2.5 as the resolution varies by a factor of 64. Plots of HFBS and DCS data at all Q values and measured temperatures (not displayed here) resemble those in Fig. 2 in terms of the quality of the fits.

The fact that the quasielastic portions of the spectra for all Q values at resolutions ranging from 1 to 64 μeV are well described by the same hopping parameter at a given temperature lends credibility to the basic correctness of

applying the Chudley–Elliott model to this system. As discussed above, detailed MC calculations that reproduce the results of previous MC studies [7] which display hopping correlations at higher concentrations show that they have little effect on the lineshape at this concentration. An Arrhenius plot of r vs. $1/T$ yields a value of the activation energy $0.30 \pm 0.02 \text{ eV}$, in good agreement with that obtained by NMR measurements on the $\text{ZrBe}_2\text{H}_{1.4}$ system ($0.27 \pm 0.02 \text{ eV}$) [8]. This agreement suggests that hydrogen concentration plays only a small role in modifying the average potential energy landscape experienced by the H ions as they diffuse about.

H may be trapped in various kinds of defect sites that surely exist in this powder sample. However, the issue of the observed weak dependence of the elastic-like fraction f on instrument, or on resolution with a given instrument remains unresolved.

5. Conclusion

The present neutron quasielastic scattering measurements on a single-phase $\text{ZrBe}_2\text{H}_{0.56}$ sample having the AlB_2 structure made on two spectrometers with widely differing resolutions can be successfully interpreted in terms of a simple two-parameter model at each temperature for all momentum transfers measured. This model incorporates 2-D n.n. uncorrelated, activated H hopping along with an extra elastic-like term to account for an H fraction that is relatively immobile on the time scales measured. A single τ accounts for the quasielastic data at all resolutions for all Q values measured at a given temperature. The activation energy is inferred to be $0.30 \pm 0.02 \text{ eV}$, in agreement with NMR results for $\text{ZrBe}_2\text{H}_{1.4}$.

References

- [1] A.F. Andresen, K. Otnes, A.J. Maeland, *J. Less-Common Metals* 89 (1983) 201.
- [2] Prompt gamma measurements courtesy of R. Paul of the NIST Analytical Chemistry Division, Nuclear Methods Group.
- [3] C.T. Chudley, R.J. Elliott, *Proc. Phys. Soc. Lond.* 77 (1961) 353.
- [4] J.M. Rowe, Kurt Sköld, H.E. Flotow, J.J. Rush, *J. Phys. Chem. Solids* 32 (1971) 41.
- [5] R. Hempelmann, *Quasielastic Neutron Scattering and Solid State Diffusion*, Oxford University Press Inc., NY., 2000, pp. 131–139.
- [6] <<http://www.ncnr.nist.gov/dave>>.
- [7] R. Kutner, *J. Phys. C: Solid State Phys.* 18 (1985) 6323.
- [8] A.F. McDowell, C.F. Mendelsohn, M.S. Conradi, R.C. Bowman Jr., A.J. Maeland, *Phys. Rev. B* 51 (1995) 6336.